PB83-225805

Analysis of Individual Hydrocarbon Species in Ambient Atmospheres Techniques and Data Validity

(U.S.) Environmental Sciences Research Lab.
Research Triangle Park, NC

1983

U.S. Department of Commerce
National Technical Information Service
NTIS

PB83-225805

EPA-600/D-83-074

ANALYSIS OF INDIVIDUAL HYDROCARBON SPECIES IN AMBIENT ATMOSPHERES: TECHNIQUES AND DATA VALIDITY

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TECHNICAL REPORT DATA (Please read Instructions on the reverse before completing)		
1. REPORT NO. EPA-600/D-83-074	2.	3. RECIPIENT'S ACCESSION NO. PB85 225805
4. TITLE AND SUBTITLE ANALYSIS OF INDIVIDUAL HYDROCARBON SPECIES IN AMBIENT ATMOSPHERES: TECHNIQUES AND DATA VALIDITY		5. REPORT DATE 1983
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) H. H. Westberg, W. A. Lonneman, and M. W. Holdren		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Washington State University College of Engineering Pullman, Washington 99164		10. PROGRAM ELEMENT NO. CDWA1A;02 - 0323
		11. CONTRACT/GRANT NO. CR 806683
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Sciences and Research Laboratory, RTP, NC Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, NC 27711		13. TYPE OF REPORT AND PERIOD COVERED
		14. SPONSORING AGENCY CODE EPA/600/09
15. SUPPLEMENTARY NOTES		

16. ABSTRACT

During the summer of 1980, EPA sponsored a large field program which was designed to gather data for developing and testing a regional scale oxidant model. Individual hydrocarbons were measured over a 30 day period in Boston, New York, Washington, DC, Baltimore, and Columbus, Ohio. The widespread nature of the hydrocarbon sampling network necessitated the participation of three gc analyses groups: Washington State University (WSU); Battelle Columbus Laboratories; and the Gas Kinetics and Photochemistry Branch (GKPB) of the Environmental Sciences Research Laboratory. In order to ensure intercomparability of results, a hydrocarbon quality assurance program was utilized. Two methods for comparison were used; the periodic analysis of synthetic mixtures and the shared analysis of ambient air samples. This report presents the results of this quality assurance program.

17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS (This Report) UNCLASSIFIED	21. NO. OF PAGES 24
	20. SECURITY CLASS (This page) UNCLASSIFIED	22. PRICE

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INTRODUCTION

Interest in the hydrocarbon composition of urban and rural atmospheres has increased in recent years due to the development of sophisticated air quality simulation models which require individual hydrocarbon species information. The measurement of individual species concentration is a complex process involving several steps. Air samples are normally collected in a plastic bag or rigid metal container. A measured volume of air is then removed from the collection container and passed through a cryogenic trap to concentrate the organic species. The actual analysis is accomplished by transferring the contents of the cryogenic trap into a gas chromatographic system. Very little quality assurance work has been performed in order to evaluate the precision and accuracy of this analytical procedure. Potential problem areas include loss of organic components to the walls of the collection container, breakthrough of the most volatile gases during the concentration step, incomplete transfer of the higher molecular weight components from the cryogenic trap and the usual calibration, resolution and peak area integration uncertainties associated with gas chromatography.

During the summer of 1980, EPA sponsored a large field program which was designed to gather data for developing and testing a regional oxidant model. Individual hydrocarbons were measured over a thirty day period in Boston,

Washington, DC, Baltimore, Newark, NJ and Columbus, OH. The widespread nature of the hydrocarbon sampling network necessitated the participation of three research groups: Washington State University (WSU); Battelle Columbus Laboratories; and the Gas Kinetics and Photochemistry Branch (GKPB) of the Environmental Sciences Research Laboratory, U.S. Environmental Protection Agency. WSU operated a laboratory in Newark, NJ and two in Baltimore (where samples from Baltimore and Washington, DC were analyzed). Battelle operated in Boston and GKPB set up facilities in Columbus.

In order to ensure intercomparability of results, a hydrocarbon quality assurance program was instituted. Two methods for intercomparing hydrocarbon results were utilized. One procedure consisted of intermittent sampling of an artificially prepared standard gas mixture. The synthetic mixture contained fourteen hydrocarbon components at concentrations ranging from about 15 to 25 ppbC. The mixture was prepared by GKPB and distributed in 6 liter passivated (Summa process) stainless steel containers. The synthetic gas mixture was analyzed approximately twice a week during the 4 week period.

The second method utilized for interlaboratory comparison entailed the exchange of ambient samples among the laboratories. Each analytical group collected an ambient air sample in a treated stainless steel canister, analyzed it and sent it to another laboratory which in turn analyzed the sample and sent it along to the next group. In this fashion, each ambient sample was analyzed by each participating laboratory. This program was referred to as a "round robin" analysis since each group analyzed the same sample.

It was felt that a QA program of this type would provide information about both precision and accuracy. Precision data would be generated by the repeated analysis of the same synthetic standards. A measure of accuracy

would be gained by the intercomparison of results when the same sample was analyzed by five different laboratories. This method for determining accuracy was deemed appropriate because the usual procedure which involves the use of a NBS traceable standard is unsatisfactory. Certified propane standards at concentrations greater than 5 ppmC are provided by the NBS. This is about 3 orders of magnitude larger than the concentrations at which this hydrocarbon is normally encountered in ambient air. Consequently, in order to run the NBS standards, instrument parameters must be changed significantly and sample size must be greatly reduced. In addition, propane cannot be used with certain GC columns due to its very short elution time.

EXPERIMENTAL

Several similarities existed in the analytical systems and procedures utilized by the five laboratories. All of the research groups employed commercial GC systems equipped with flame ionization detectors, a computerized data acquisition system and a cryogenic concentration step. GC column types constituted the main procedural difference. GKPB utilized a three column system for resolving the C_2-C_{10} hydrocarbon fraction while WSU and Battelle employed only two columns. WSU and Battelle used the same type of column (SE-30 capillary) for analyzing the C_5-C_{10} fraction; otherwise, all of the columns used by the three groups were different. Table 1 summarizes the GC conditions employed by the three research groups.

Gas Chromatographic Analysis

GKPB. Three chromatographic columns were used to analyze the C_2-C_{10} hydrocarbons. The C_2-C_5 hydrocarbons (excluding the C_4 and C_5 olefins) were

Table 1. Summary of GC Conditions Utilized by the Three Research Groups

Hydrocarbons	Column	Oven Temp.
EPA-GKPB		
C_2-C_5 (ex. C_4-C_5 olefins)	packed (silica gel)	25°C (isothermal)
C_4-C_8 (non-aromatic)	SCOT (dibutylmaleate)	~0°C (isothermal)
C_6-C_{10} (aromatic)	SCOT (m-bis-m-phenoxybenzene)	80°C (80°-110°C @ 10°/min)
BATTELLE		
C_2-C_5	packed capillary (phenylisocyanate/Porasil C)	35°C (isothermal)
C_4-C_{10}	fused silica WCOT (SE-30)	-50° to 100°C @ 8°/min
WSU		
C_2-C_5	packed capillary (n-octane/Porasil C)	-60° to 80°C @ 24°/min
C_5-C_{10}	glass capillary (SE-30)	-50° to 80°C @ 4°/min

separated on a 2.4 m x 3 mm stainless steel column packed with 60/80 mesh silica gel grade 58 (Grace Laboratories, Baltimore, Maryland). The column was maintained at room temperature 25° ± 2°C with a helium carrier gas flowrate of 40 cm^3/min. The C_4-C_8 aliphatic hydrocarbons were separated on a 15.2 m x 0.51 mm i.d. SCOT column coated with dibutyl-maleate. This column was maintained at ice water temperature. The helium carrier gas flowrate was 8 cm^3/min.

A 30.5 m x 0.51 mm i.d. SCOT column coated with m-bis m-phenoxy benzene was used to separate the C_6-C_{10} aromatic hydrocarbons. The column was initially maintained at 80°C for 20 min. and then temperature programmed to 110°C at 10°C/min. during the final stages of the analysis. The carrier gas flowrate was maintained at 8 cm^3/min.

Battelle Laboratories. Light hydrocarbons were analyzed on a Varian 3700 gas chromatograph which was operated isothermally at 35°C. A 1/16 in. O.D. by 20 ft. nickel column filled with phenylisocyanate/Porasil C was employed for separating the individual hydrocarbons. A 50 meter SE-30 fused silica wall coated column (Hewlett Packard) provided separation for the C_4 through C_{10} hydrocarbons. These analyses were accomplished with a Hewlett Packard 5711 gas chromatograph. Subambient temperature programming from -50° to +100°C at 8 degrees per minute provided good resolution and stable baselines.

WSU. Gas chromatographic analyses were performed with Perkin Elmer and Hewlett Packard chromatographs equipped with subambient temperature programming capabilities. The column used to separate light hydrocarbons (C_2-C_6) was a packed capillary (20' x 1/16") containing Durapak n-Octane/Porasil C. When operated with a carrier gas (He) flow of 5 cm^3/min and temperature programmed from -60° to 80°C at 24°/min, this column provided excellent resolution of the light

hydrocarbon fraction. A SE-30 glass capillary column (J & W Scientific) was used to separate hydrocarbons in the C_5 to C_{10} molecular weight range. Helium was used as the carrier gas with column flow maintained at 1 cm^3/min. Optimum results were obtained by temperature programming from -50° to 80°C at 4°/min.

GC Calibration

Procedures employed by the three research groups for calibrating their gas chromatographs are described in the following paragraphs.

Battelle utilized an 8.64 ppmC "certified" NBS propane standard as their basis for calibration. By directly injecting 75, 100, and 150 cc quantities of this standard into their light hydrocarbon system, a best fit relationship between area response and volume injected was obtained. Upon extrapolating the best fit line to 300 cc volume, an area response factor for 8.64 ppmC was calculated. When this factor was multiplied by the area counts recorded for individual hydrocarbons in a 300 cc ambient sample, concentrations were obtained in units of ppbC. Battelle's heavy hydrocarbon system (C_4-C_{10}) was calibrated using a transfer standard. A pentane-air mixture was prepared and the pentane concentration was established on the light hydrocarbon system as described previously. Various volumes of the pentane standard were then injected into the heavy hydrocarbon system and an area response per ppbC factor was calculated. This factor was used to convert area responses of the individual species in ambient samples to concentration units (ppbC).

The GKPB group utilized a mixture of hydrocarbons as their absolute standard. The standard was prepared by injecting a measured volume of each liquid hydrocarbon into a known volume of air. The gaseous hydrocarbon concentration was then calculated using the ideal gas law. Additional dilutions

were then made until the hydrocarbon concentration approached the range normally encountered in ambient air (~30 ppbC). The mixture containing hydrocarbons of known concentration was then run on each of the three GC systems employed by GKPB. Area response per ppbC factors were calculated for each hydrocarbon and then the response factors were averaged to give one factor for converting area response to concentration units. This mixture usually contained 12-15 selected C_2-C_9 hydrocarbons to permit at least 5 chromatographic peaks on each GC column. Using this procedure, individual hydrocarbon species in ambient samples are reported in units of ppbC.

Washington State University calibrated with a 0.204 ppm 2,2-dimethylbutane standard purchased from Scott Environmental Technology, Inc. The 0.204 ppm concentration was verified in the WSU laboratory through comparison with n-hexane standards prepared by a static dilution procedure similar to the procedure utilized by GKPB to prepare their absolute calibration standard. The 2,2-dimethylbutane is compatible with both columns used by WSU for their hydrocarbon analyses. Measured volumes of the standard were injected into the gas chromatograph. From the recorded area responses, a graph was constructed which related area counts to weight of 2,2-dimethylbutane injected. An area count per nanogram factor was determined which was used to convert peak areas in an ambient air chromatogram to nanograms of hydrocarbon. Since the volume of sample air is carefully measured, the concentration of each hydrocarbon can be calculated in units of $\mu g/m^3$.

It is obvious from the foregoing discussion of calibration techniques that none of the research groups attempted to determine response factors for each of the hydrocarbon species present in ambient atmospheres. Consequently, the assumption must be made that relative sensitivities are the same for all hydrocarbons. This is not absolutely true but the work of Dietz [1] has shown

that relative responses for the majority of species that contain only carbon and hydrogen vary by only about 5%. Thus, the assumption is made that the flame ionization detector response for a fixed amount of hydrocarbon is the same for all species. Needless to say, it would be impractical to try to determine individual response factors for the one hundred or so peaks that are normally recorded in an urban air sample.

RESULTS AND DISCUSSION

Two different types of samples were utilized in the 1980 quality assurance program. A synthetic QC standard was prepared by GKPB which contained a mixture of paraffinic, olefinic and aromatic hydrocarbons at concentrations commonly encountered in urban atmospheres. Table 2 provides a listing of the hydrocarbons and the concentrations assigned by GKPB. The second type consisted of ambient air samples collected at the field sites that were circulated to the participants via a round robin exchange procedure.

Synthetic QC Standard Results

The synthetic QC mixture listed in Table 2 was used to test each laboratory's identification and quantitation capabilities as well as the precision of their analytical system. It consisted of a "blind" standard to all laboratories except GKPB in Columbus because the contents and concentrations were not revealed by GKPB. As mentioned previously, this mixture was analyzed repeatedly by each group throughout the study period. Table 3 shows results obtained by the Battelle laboratory in Boston. These data exemplify the results reported by the other groups.

Table 2. Composition and Concentration (ppbC) for QC Mixture Prepared by GMPB for the 1980 Intercomparison Study.

Component	Conc.	Conponent	Conc.
Ethane	19.4	3-Methylpentane	17.5
Ethylene	21.1	1-Hexene	17.6
Propane	21.2	Benzene	21.0
Propene	18.4	Toluene	20.5
n-Butane	22.8	o-Xylene	16.5
1-Pentene	26.1	n-Propylbenzene	14.2
2-Methylpentane	17.2	1,2,4-Trimethylbenzene	14.2

Table 3. Individual Hydrocarbon Concentrations (ppbC) Measured by Battelle in QC Mix.

	Date Analyzed									
	7/24	8/6	8/8	8/16	8/18	8/24	8/28	8/29	Ave.	SD(±)
ETHANE	18.3	18.0	18.4	19.0	19.9	18.3	18.1	18.7	18.6	0.6
ETHYLENE	19.8	19.7	19.7	20.7	21.6	19.8	19.7	20.4	20.2	0.7
PROPANE	20.3	20.3	20.5	21.5	22.0	20.3	20.1	21.1	20.8	0.7
PROPENE	21.6	19.2	19.3	20.0	20.3	18.8	18.5	18.9	19.6	1.0
n-BUTANE	19.2	21.4	21.8	22.5	23.5	21.3	21.7	22.0	21.7	1.2
1-PENTENE	*	*	*	*	*	*	*	*	*	*
2-METHYLPENTANE	17.1	16.6	16.7	17.2	17.4	17.2	17.1	16.9	17.0	0.3
3-METHYLPENTANE	18.1	17.2	18.1	17.8	17.9	17.9	17.7	17.6	17.8	0.3
1-HEXENE	17.4	16.4	16.4	16.4	16.2	15.3	14.6	14.3	15.9	1.0
BENZENE	19.4	19.1	19.1	20.0	22.0	19.9	19.6	19.7	19.9	0.9
TOLUENE	21.9	21.2	20.5	21.5	21.8	20.7	20.4	19.9	21.0	0.7
o-XYLENE	15.8	13.5	12.6	11.1	10.8	8.2	6.9	6.6	10.7	3.3
n-PROPYLBENZENE	9.6	7.1	5.6	4.2	3.6	5.0	1.5	1.3	4.7	2.8
1,2,4-TRIMETHYLBENZENE	5.5	1.9	1.2	0.6	0.7	0.4	3.4	0.7	1.8	1.8

* Not reported due to interference with a sample canister impurity thought to be acetone.

There are several features in Table 3 that warrant comment. In nearly all cases, the hydrocarbon species were correctly identified and the reported concentrations were comparable to those assigned by GKPB. This was especially true for the C_2-C_4 hydrocarbon species. 1-Pentene was not reported due to interference with a sample canister impurity thought to be acetone. It can be seen that standard deviations for most of the hydrocarbons are small compared to the reported concentrations. Excellent reproducibility existed for all except the three C_8 and C_9 aromatic species. The coefficient of variation (SD/mean) was less than 7% for all species in the C_2-C_7 molecular weight range. Reasons for the much poorer precision with o-xylene, n-propylbenzene and 1,2,4-trimethylbenzene were investigated following the study. Analytical problems such as incomplete transfer of these less volatile species from the cryogenic trap to the GC column were first considered but subsequently found to be unlikely. A closer examination of the data revealed an apparent decrease in concentration of these three species with time. This can be seen in Table 3 where the reported values for o-xylene decreased from an initial value of 15.8 ppbC to 6.6 ppbC at the end of the study period. This implied that these aromatic compounds were being lost within the sample containers. This was verified in subsequent tests by the GKPB group. The sample container used by Battelle during the field study period was thoroughly cleaned and refilled with the QC mixture in September. As shown in Table 4, the concentration of the three aromatic species had decreased significantly by the middle of December while the concentration of the lower molecular weight hydrocarbons remained essentially unchanged. The decrease of o-xylene observed by GKPB was not as large as that observed by Battelle. There is no clear explanation for this difference.

A comparison of the average concentrations reported by Battelle in Table 3 with the assigned concentrations in Table 2 reveals good agreement if o-xylene,

Table 4. Results of Stability Test of Hydrocarbons in QC Mixture (Canister used by Battelle)

Compound	Concentration (ppbC)		
	9/25/80	10/3/80	12/16/80
Ethane	19.3	18.9	19.5
Propene	19.5	18.9	19.4
Butane	22.8	22.3	22.7
o-Xylene	14.3	14.7	10.2
n-Propylbenzene	12.9	12.5	4.8
1,2,4-Trimethylbenzene	14.7	11.2	0.3

Table 5. Mean Concentration (ppbC) and Standard Deviation for Components of the QC Mixture as Determined by the Various Laboratories During the Field Study.

	WSU-BALT	WSU-WASH	WSU-NY	BATTELLE	GKPB	ALL DATA
ETHANE	16.5 ± 0.9	17.6 ± 1.4	17.9 ± 2.5	18.6 ± 0.6	19.4 ± 0.9	18.0 ± 1.7
ETHYLENE	18.0 ± 1.2	18.7 ± 0.6	20.1 ± 1.6	20.2 ± 0.7	21.2 ± 1.8	19.7 ± 1.6
PROPANE	20.9 ± 1.3	19.9 ± 1.6	20.1 ± 1.7	20.8 ± 0.7	21.3 ± 1.3	20.6 ± 1.4
PROPENE	18.2 ± 1.2	18.4 ± 0.7	20.7 ± 1.8	19.6 ± 1.0	21.7 ± 1.2	19.7 ± 1.8
n-BUTANE	22.3 ± 1.4	20.0 ± 0.7	22.4 ± 2.2	21.7 ± 1.2	19.0 ± 0.6	21.1 ± 1.9
1-PENTENE	17.3 ± 4.7	20.4 ± 2.4	24.7 ± 2.2	--	26.1 ± 0.7	22.3 ± 4.4
2-METHYLPENTANE	14.9 ± 2.0	14.0 ± 1.7	15.6 ± 1.1	17.0 ± 0.3	17.2 ± 0.6	15.7 ± 1.7
3-METHYLPENTANE	15.3 ± 2.4	13.3 ± 1.8	16.1 ± 1.0	17.8 ± 0.3	17.5 ± 0.3	16.2 ± 1.9
1-HEXENE	15.1 ± 2.7	12.7 ± 2.0	15.3 ± 1.3	15.9 ± 1.0	17.6 ± 0.7	15.1 ± 2.8
BENZENE	17.1 ± 3.3	11.5 ± 1.7	17.6 ± 1.4	19.9 ± 0.9	20.3 ± 2.3	17.3 ± 3.5
TOLUENE	17.1 ± 3.7	--	19.0 ± 1.0	21.0 ± 0.7	20.5 ± 1.3	19.3 ± 2.5
o-XYLENE	12.7 ± 2.9	--	10.7 ± 3.3	10.7 ± 3.3	15.7 ± 0.8	12.2 ± 3.4
n-PROPYLBENZENE	10.5 ± 3.3	--	4.6 ± 3.2	4.7 ± 2.8	13.8 ± 1.1	8.1 ± 4.7
1,2,4-TRIMETHYLBENZENE	9.6 ± 3.3	--	4.1 ± 3.5	1.8 ± 1.8	14.3 ± 1.1	7.1 ± 5.4

n-proplybenzene and 1,2,4-trimethylbenzene are ignored. This is further exemplified in Table 5 where the means and standard deviations for the QC mixture are shown for all the laboratories. The ALL DATA column, which represents a total of about 40 analyses (~8 by each of the five groups), demonstrates good agreement between the various laboratories. The coefficient of variation is less than 12% for all of the paraffinic and low molecular weight olefinic species. The problem with the C_8 and C_9 aromatics is once again evident in the "ALL DATA" compilation with coefficients of variation ranging between 28 and 76%. There is also an apparent problem with 1-pentene and 1-hexene since the standard deviations for these two species are relatively large in relation to the mean values.

A close examination of Table 5 shows that the WSU laboratories systematically report lower average hydrocarbon concentrations in the QC mixture than Battelle and GKPB. In order to intercompare results of the QC analysis it was necessary to employ a common set of concentration units. As described in the Experimental Section, the Battelle and GKPB groups calibrated their chromatographs in volume concentration units (area response/ppbC) while the WSU laboratories all calibrated in terms of mass (area response/ng). For comparative purposes, the WSU hydrocarbon concentrations have been converted from $\mu g/m^3$ units to ppbC. A problem exists in selecting the most suitable conversion factor(s). Through the use of the ideal gas law, the following expression can be derived for interconversion between volume and mass concentration units:

$$\mu g/m^3 = ppm \times \frac{\text{molecular weight}}{RT} \times 10^3 \qquad (1)$$

By definition, ppm is equal to ppmC divided by the number of carbon atoms in the molecule. Thus, equation (1) can be rewritten as

$$\mu g/m^3 = ppmC \times \frac{1000}{RT} \times \frac{\text{molecular weight}}{\text{number of carbon atoms}} \qquad (2)$$

It is obvious from equation (2) that for a fixed volume concentration (ppbC) the mass concentration $\mu g/m^3$ will vary from hydrocarbon to hydrocarbon because the molecular weight/number of carbon atoms ratio is not constant for all hydrocarbons (e.g. methane = 16.0, ethane = 15.0, benzene = 13.0, etc.)

WSU utilized a factor of 1.5 for converting from $\mu g/m^3$ to ppbC. This factor was chosen for the following reasons: a) it is impractical and in some cases impossible to use a separate conversion factor for each individual hydrocarbon peak that appears in an ambient air chromatogram, b) an average factor could be employed based on several of the most abundant species; however, this would vary from sample to sample and would have to be clearly defined in some manner, c) the 1.5 factor is derived from methane at 1 atm pressure and 25°C. This factor was used by GKPB for interconverting between $\mu g/m^3$ and ppmC units when the recommended Air Quality Standard for hydrocarbons was published [2].

The foregoing discussion is apropos because if WSU had used a conversion factor specific for each hydrocarbon in the QC mixture their reported concentrations would be larger. For example, the average values reported for ethane in Table 5 would be 17.9, 19.1 and 19.4 for WSU-Balt, WSU-Wash and WSU-NY, respectively. Obviously, the systematic difference in reported hydrocarbon concentrations is eliminated if conversion factors specific to each hydrocarbon are employed.

Round Robin Analyses

The round robin program consisted of the exchange of ambient air samples collected by each participating laboratory. On day one, each laboratory filled a sample canister with sufficient ambient air for five hydrocarbon analyses. An analysis of the ambient sample was performed immediately after collection

and the canister was then sent (air freight) to another laboratory. The sample was generally delivered to the second laboratory during the next day. It was analyzed on the day received and sent to the third group. Thus, five different samples were analyzed by each of the five laboratories over a period of about 10 days. Of the twenty samples circulated in this manner during the 4 week study period, analyses for 16 were essentially complete. Insufficient pressure in the other samples presented a complete round robin analysis.

An enormous amount of data was acquired from the round robin program. Table 6 provides a typical example of an individual hydrocarbon data report. The 48 species that were identified in this sample account for 91% of the hydrocarbon content. The percentage of unidentified compounds was similar between the five research laboratories and usually fell in the range of 8-15%.

The mean values for total NMOC in the 16 round robin samples ranged from 36.3 to 1985 ppbC. The coefficient of variation ranged from 3.7 to 21.0% with the average being 10.6%. Since the reproducibility of the gas chromatographic methods utilized is typically ±10%, the round robin analysis program indicates that there were not significant differences between total NMOC results reported by the five laboratories.

Table 7 shows a summary of data acquired by the five laboratories for round robin sample 3 collected in Baltimore. It can be seen that there was excellent agreement between the five laboratories for total nonmethane hydrocarbon concentration. The mean value for the five analyses was 530 ppbC with a standard deviation of ±31 ppbC. Summations of the paraffinic and aromatic content exhibit a coefficient of variation of less than 10%. Also, the variation in reported concentrations for most of the individual species shown in Table 7 is small. However, there are some notable exceptions to the generally good conformity. A relatively large coefficient of variation is

Table 6. Individual Hydrocarbon Concentrations (ppbC) Measured by WSU-NY in QA Sample 3 Collected by WSU-Baltimore

ppbC	Hydrocarbon	ppbC	Hydrocarbon
13.7	Ethane	6.0	Methylcyclopentane
24.1	Ethylene	6.6	2,4-Dimethylpentane
19.0	Acetylene	11.3	Benzene
14.0	Propane	1.9	Cyclohexane
9.2	Propene	3.4	2-Methylhexane
14.9	i-Butane	5.3	2,3-Dimethylpentane
43.8	n-Butane	7.1	3-Methylhexane
2.2	1-Butene	6.6	2,2,3-Trimethlpentane
3.0	i-Butene	5.7	n-Heptane
3.6	t-2-Butene	4.2	Methylcyclohexane
53.0	i-Pentane	53.8	Toluene
24.8	n-Pentane	4.5	2-Methylheptane
1.9	1-Pentene	2.6	3-Ethylhexane
1.4	t-2-Pentene	2.4	n-Octane
0.8	c-2-Pentene	11.3	Ethylbenzene
1.4	2-Methyl-2-Butene	23.1	p & m-Xylene
2.3	Cyclopentane	0.6	Styrene
1.2	3-Methyl-1-Butene	7.6	o-Xylene
16.1	2-Methylpentane	2.3	n-Nonane
5.8	Isoprene	1.0	n-Propylbenzene
11.6	3-Methylpentane	8.5	p-Ethyltoluene
2.1	2,2-Dimethylbutane		m-Ethyltoluene
15.1	n-Hexane	8.6	1,2,4-Trimethylbenzene
3.7	2,3-Dimethylbutane	3.1	n-Decane

Total Identified Hydrocarbons	ppbC	%
Olefin	54.6	12
Aromatic	126	26
Paraffin	277	58
Acetylene	19.0	4
	477	

	ppbC
Total Unidentified Hydrocarbons	48
Total NMHC by summing individual species	525

Table 7. Comparison of Various Hydrocarbon Concentrations (ppbC) Reported for QA Sample 3 Collected By the WSU-Baltimore Laboratory

	WSU Balt.	WSU Wash.	WSU NY.	Batt.	GKPB	Mean	SD	CV %
Ethane	12.0	13.0	13.7	14.0	14.5	13.2	.9	6.8
Ethylene	22.5	23.0	24.1	26.8	25.0	24.3	1.7	7.0
Propane	16.0	13.5	14.0	14.2	14.0	14.3	1.0	7.0
Propene	8.5	7.5	9.2	8.3	8.7	8.4	.6	7.1
n-Butane	43.6	38.5	43.8	45.1	42.3	42.7	2.5	3.9
2-Methylpentane	16.0	17.0	16.1	17.7	20.5	17.5	1.8	10.3
3-Methylpentane	11.5	12.0	11.6	12.6	13.1	12.2	.7	6.7
1-Pentene	5.0	-	1.9	-	1.3	2.7	2.0	74.0
1-Hexene	-	-	-	-	1.0	1.0	-	-
Benzene	11.5	11.0	11.3	12.9	25.5	14.4	6.2	43.0
Toluene	47.0	48.5	53.8	54.6	46.5	50.1	3.8	7.6
o-Xylene	8.0	10.5	7.6	9.6	9.1	9.0	1.2	13.3
n-Propylbenzene	-	-	1.0	1.9	1.9	1.6	.5	31.3
1,2,4-Trimethylbenzene	4.0	2.5	8.6	9.2	6.6	6.2	2.9	46.8
Total NMOC	534	487	525	575	527	530	31	6
Sum of Paraffins	282	266	296	291	285	284	11	4
Sum of Olefins	48	37	55	38	63	48	11	23
Sum of Aromatics	120	137	126	136	141	132	9	7

apparent in the summation of olefins and for the individual C_5 and C_6 olefins. The interlaboratory agreement was normally very good for ethylene and propene but generally quite poor for the C_4, C_5 and C_6 olefins. This discord in the C_4-C_6 olefin analysis appears to be the result of concentrations near the detection limits of the analytical instrumentation and difficulties with completely resolving these species on some of the analytical columns that were utilized. Olefins normally constitute less that 10% of the hydrocarbon total and, therefore, the relatively large variation associated with this class of compounds has little influence on the total hydrocarbon concentration. Accurate quantitation of ambient olefins is important, however, because they are easily oxidized in the atmosphere and play an important part in smog producing reactions.

Table 7 indicates a problem with benzene analysis, as well. The relatively large standard deviation for benzene is due to the high value reported by GKPB. If this were considered as an outlier point and, as such, eliminated from the data set, good agreement between the remaining four labs would exist. However, examination of the reported benzene concentrations for all sixteen round robin samples shows that the GKPB results are nearly always higher by a factor of about 1.7 than the mean for all the laboratories. It is interesting to note that this discrepancy is not as pronounced in the analysis of the synthetic QC standards. For example, Battelle and GKPB reported nearly identical benzene concentrations (19.9 vs 20.3 ppbC) after repeated analysis of the QC mixture (see Table 5). This would imply that other organics in the ambient air samples are interfering with benzene resolution on the GKPB chromatographic column. These examples serve to point out that while there is good agreement between all laboratories for many of the individual hydrocarbon species present in ambient atmospheres, quantitation difficulties do exist for certain olefinic and aromatic species.

SUMMARY AND CONCLUSIONS

It is extremely difficult to prepare and store absolute hydrocarbon standards at low ppb levels. Furthermore, it is difficult to reference instrument performance to a NBS standard when the gas chromatograph is operated in a mode appropriate for measuring ambient hydrocarbon levels. Therefore, normal accuracy determination procedures can not be applied to hydrocarbon analysis. In lieu of this, the sample exchange program described herein was established for estimating the accuracy of ambient hydrocarbon measurement methods. Five laboratories using the same instrumental method (gas chromatography) but with differing analytical procedures, showed an average coefficient of variation of 11% in total NMOC concentrations. In our judgment, this provides the best estimate of hydrocarbon measurement accuracy.

Based on the results of this QA program several recommendations can be advanced for establishing the validity of individual hydrocarbon data. First of all, it is absolutely essential to have some form of QA program that involves an interchange of samples between several laboratories. The QA sample analysis should begin before any ambient air measurements are made. An examination of results from these preliminary analyses is essential in order to confirm the performance capabilities of each participant. If any changes are required for accurate analysis, they can then be made prior to the start of ambient data collection. Synthetic QC mixtures are perhaps the best type of sample to use for this purpose. Composition and concentration information should be unknown to the participating laboratories and all QC samples should be interchanged between analysis labora ories. In the studies described herein, separate QC samples were sent to each participating laboratory. Even though these canisters were passivated, some storage losses occurred. If the

QC mixtures are exchanged, surface losses will be confirmed by each participant.

One QA sample should be analyzed each day to insure the quality of the data base. During the 1980 program, the hydrocarbon analysis groups were intermittently deluged with large numbers of ambient samples. On several occasions, the daily QA sample analysis was omitted due to time constraints.

A large data base coupled with an exchange of QA results during various stages of the program will help identify inconsistencies and improve data quality. For example, it was pointed out previously that analytical problems existed in the measurement of olefins. Steps could have been taken to correct this deficiency if it had been recognized prior to completion of the field program.

ACKNOWLEDGEMENTS

Funds for this research study were furnished by the Environmental Protection Agency, Environmental Sciences Research Laboratory, Research Triangle Park, NC.

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